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A Model of Nematic Liquid Crystals for Viscosity and Self-diffusion

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A Geometrical model is presented which rationalizes the viscosity and self-diffusion coefficients and their anisotropies in nematic liquid crystals. The model is an extension of Eyring's theory of the liquid state to the anisotropic fluid, based on the geometry of the constituent molecule. A novel concept, effective anisotropy factor of a molecule, is introduced which is determined from the viscosity coefficients. An empirical law on the principal viscosity coefficients by Kneppe *et al.* is given its molecular basis by this model. Self-diffusion coefficient tensor calculated from the available viscosity data of PAA, MBBA, and HBAB agree well with experiment.

General understanding of cohesion of organic molecules shows that the nature of mesophases which appear between the rigid molecular crystal and the isotropic liquid is essentially determined by the geometrical characteristics of the constituent molecules: The liquid crystalline mesophase is formed by a rodlike molecule having a certain degree of internal rigidity,[1] whereas the special kinds of mesophases such as discotic or columnar ones are formed by a disk-like molecule[2] and the plastic crystal consists of a globular molecule.[3] One is thus tempted to develop a model theory of such mesophases, which will help to understand their features at least qualitatively like the one presented here for viscosity and self-diffusion in the nematic liquid crystal, the most typical mesophase formed by rodlike molecules.

Since Miesowicz[4] pointed out that external magnetic field has an effect on the viscosity of 4,4′-dimethoxyazoxybenzene (PAA) in 1935, the flow properties of nematic liquid crystals have been one of the interesting problems in rheology[5] and molecular dynamics.[6] Continuum theory of the viscoelastic properties of nematic liquid crystal was developed by Ericksen and Leslie.[7] On the basis of their theory, Lubensky[8] proposed relations between Franck's elastic constants and the nematic order parameter, $\langle p_2 \rangle$, and later, Imura and Okano[9] derived phenomenological relations between $\langle p_2 \rangle$ and viscosity coefficients. These theories could, however, interpret the experimental data with only partial success.[10] Recently, a comparative experimental study of the viscosity coefficients of some nematic liquid crystals were carried out by Kneppe *et al.*[11] and some rules concerning relationship among the principal viscosity coefficients were found in a purely empirical manner.

Our standpoint is very different from the models of the former authors; it is not an elastic continuum theory but a very simple model theory based on the geometrical characteristic of the constituent molecule. Our treatment has its origin in Eyring's theory of the rate processes[12] and of significant liquid structure,[13] and is an extension of Eyring's theory of the liquid state to the system of uniaxial symmetry. We will describe in this paper how the anisotropic shape of the molecule is reflected on anisotropies of the diffusion coefficient tensor and of the viscosity coefficients and will derive phenomenological relations between diffusion and viscosity coefficients. Finally, comparisons with the experiments will be given. An empirical law recently found by Kneppe *et al.*[11] will find its molecular basis in our simple model.

Theory

The essential points of Eyring's idea are: (1) the liquid state consists of solid-like molecules and gas-like mobile molecules adjacent to the holes, (2) viscous flow and diffusion can be treated on a common physical basis by supposing that the two phenomena are the results of molecular friction when a molecule jumps into a hole. Eyring *et al.* developed their theory for isotropic liquids, and we will now treat the case of anisotropic fluid.

Diffusion coefficient tensor in a three-dimensional system is defined by the Fick's first law,

$$\boldsymbol{J} + \boldsymbol{D}\nabla c = 0. \tag{1}$$

Here, c and $\boldsymbol{J}$ denote the concentration of the diffusing solute and the flow density, respectively. If we take a coordinate system in which the z-axis is parallel to $\boldsymbol{n}$, the nematic director, the tensor $\boldsymbol{D}$ can be diagonalized according to the axial symmetry of the system,

$$\boldsymbol{D} = \begin{bmatrix} D_{\perp} & 0 & 0 \\ 0 & D_{\perp} & 0 \\ 0 & 0 & D_{//} \end{bmatrix}, \tag{2}$$

and Eq. 1 consists of two independent differential equations. If the velocity of flow is represented by $\boldsymbol{u}$, the following set of equations hold by virtue of the relation, $\boldsymbol{J}=c\boldsymbol{u}$ for the flow along the axis q_j (q denotes the generalized coordinate and j indicates a specific direction, x, y, or z):

$$c u_j + D_{jj}\frac{\partial c}{\partial q_j} = 0. \tag{3}$$

On the other hand, the viscosity of the nematic liquid crystal can be defined by the Newton's law.†† When the shear stress is applied along j on the plane perpendicular to i, the viscosity coefficient η_{ji} is represented by

$$\eta_{ji} = \frac{(F_{ji}/A_i)}{\left[\frac{\partial u_j(q_i)}{\partial q_i}\right]}, \tag{4}$$

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†† In fact, Newtonian property of nematic liquid crystals was confirmed experimentally (in Ref. 18) under ordinary rate of shear.

where F_{ji} denotes the shear force, and A_i is the area on which the shear force acts. If we consider a gas-like mobile molecule jumping into the nearby hole by overcoming the friction arising from interactions with solid-like molecules, the denominator in Eq. 4 is replaced by u_j/σ_i (σ_i is the nearest neighbor distance along i), and Eq. 4 is replaced by

$$\eta_{ji} = \frac{\sigma_i}{A_i} \cdot \frac{F_{ji}}{u_j}. \tag{5}$$

Let us now relate the viscosity coefficient to the diffusion coefficient by thermodynamic considerations. Generalized force $\boldsymbol{f}$ which is brought about by the spatial gradient of chemical potential is represented by

$$f_j = -kT\frac{\partial \ln \lambda}{\partial q_j}, \tag{6}$$

where λ is the absolute activity. Suppose that some fraction, κ_j, of this phenomenological force acts as the shear force along j on the plane perpendicular to i, *i.e.*,

$$F_{ji} = \kappa_j f_j. \tag{7}$$

The information about the local structure of the fluid system is included in the phenomenological parameter κ_j. Combinig Eqs. 3 and 5—7, one gets

$$\eta_{ji} = kT\frac{\sigma_i}{A_i} \cdot \frac{\kappa_j}{D_{jj}} \cdot \frac{\partial \ln \lambda}{\partial \ln c}, \tag{8}$$

which is an extended equation of Eyring and Ree[13] and can be applied to an anisotropic system. We will treat in this paper the high concentration limit, $\lambda = c$, which corresponds to the case of self-diffusion.

We now derive specific expressions of viscosity in nematic liquid crystals. In such an anisotropic fluid, viscosity depends on the direction of flow (j) and of the velocity gradient (i) with respect to the orientation of the director, $\boldsymbol{n}$. Miesowicz[14] first gave definitions of the three principal viscosity coefficients corresponding to the cases in which $\boldsymbol{n}$ is (1) parallel to the velocity gradient, (2) parallel to the flow, and (3) perpendicular to both the flow and the velocity gradient. The orientations are drawn in Fig. 1, in which η_1, η_2, and η_3 are defined by

$$\eta_1 \equiv \eta_{yz},\ \eta_2 \equiv \eta_{zy},\ \text{and}\ \eta_3 \equiv \eta_{yx},$$

corresponding to the definition by Helfrich,[15] Gähwiller,[16] and Kneppe and Schneider.[17] Note, however, the difference (η_1 and η_2 have been interchanged) from the definition by Miesowicz,[14] and Porter and Johnson.[18] An appropriate set of the geometrical factors, A_i and σ_i, are necessary to describe these viscosity coefficients through Eq. 8. We will thus introduce a very simple model treatment for these factors. The nematic liquid crystal system is regarded as an assembly of closely packed molecules having a shape of elongated regular hexagonal prism as shown in Fig. 2. We assume according to Eyring's significant structure theory that some of the molecular sites are vacant, the concentration of the holes being dependent on temperature. The symbols, a and νa, represent the dimensions of individual molecules, with ν the effective anisotropy factor of the molecular shape. This model may be called the "pencil model," by use of which A_i and σ_i can be determined from purely geometrical considerations for each of the three principal viscosity coefficients, *i.e.*, in the case of η_2, all of the six side-planes undergo a shear stress, whereas in the case of η_1, the two base hexagons, and in the case of η_3 two side-planes do, respectively. The quantity σ_i is equal to νa for η_1 whereas $\sqrt{3}\ a$ for η_2 and η_3. It will be noticed that steric hindrance is rather strong when a molecule jumps perpendicularly to $\boldsymbol{n}$ but when it jumps parallel to $\boldsymbol{n}$, the steric hindrance will be weaker and the effective forces between molecules are mainly shear forces. Therefore, we put $\kappa_z = 1$ and $\kappa_y = \kappa$, where κ remains to be determined empirically.

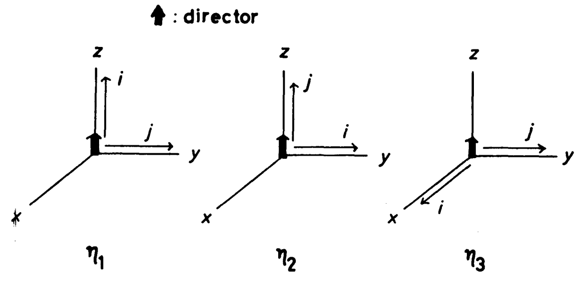

Fig. 1. Geometries for the three principal viscosity coefficients in a wall-aligned nematic liquid crystal system.

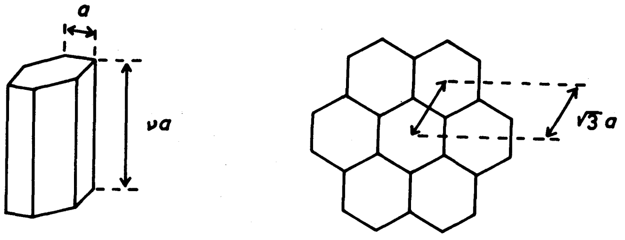

Fig. 2. Model of packing of molecules in the nematic liquid crystal.

The following set of equations are thus obtained from Eq. 8:

$$\eta_1 = \frac{\sqrt{3}\nu}{9a} \cdot \frac{\kappa kT}{D_\perp}, \tag{9}$$

$$\eta_2 = \frac{\sqrt{3}}{6\nu a} \cdot \frac{kT}{D_{//}}, \tag{10}$$

and

$$\eta_3 = \frac{\sqrt{3}}{2\nu a} \cdot \frac{\kappa kT}{D_\perp}, \tag{11}$$

which provide phenomenological relations between the viscosity and the diffusion coefficients.

A simple relation

$$\nu = 3\left(\frac{\eta_1}{2\eta_3}\right)^{1/2} \tag{12}$$

is obtained from Eqs. 9 and 11, which enables us to determine ν when the experimental data of the viscosity coefficients are available. Anisotropy of the diffusion coefficient tensor may be predicted from Eqs. 9—11 to be

$$\frac{D_{//}}{D_\perp} = \frac{\eta_3}{3\kappa\eta_2} = \frac{3\,\eta_1}{2\kappa\nu^2\eta_2}. \tag{13}$$

Comparison with Experiment

Now, comparisons of our model with experiments will be made on three typical nematic liquid crystals, 4,4′-dimethoxyazoxybenzene, *N*-(4-methoxybenzylidene)-4-butylaniline, and 4-(4-hexyloxybenzylideneamino)benzonitrile, which will be called in this paper PAA, MBBA, and HBAB according to their usual acronyms.

Table 1 lists the principal viscosity coefficients of PAA measured by Miesowicz,[14] those of MBBA by Kneppe and Schneider,[17] and those of HBAB by Gähwiller.[16] Anisotropic self-diffusion coefficients of nematic liquid crystals were first measured by Yun and Frederickson[19] for PAA by means of ^{14}C radioactive tracer technique, and later by Zupančič *et al.*[20] for MBBA by means of NMR pulsed field gradient technique coupled with multiple-pulse line-narrowing technique. The diffusion coefficients of HBAB were estimated from NMR relaxation measurements by the present authors.[21] These data are tabulated in Table 2.

Effective Anisotropy Factor of a Molecule in the Nematic State. This factor, ν, can be calculated from the data of η_1 and η_3 (Table 1) by using Eq. 12, and is shown in Table 2 for each of the three compounds. Temperature-dependences of ν in MBBA and in HBAB are also calculated††† and shown in Figs. 3 and 4, where temperatures are reduced by T_c, the clearing temperature. In these figures the temperature-dependences of the nematic orientational order parameter, $\langle p_2 \rangle$, are also shown.

Table 1. Experimental data of principal viscosity coefficients[a)]

	Temperature	Principal viscosity coefficients		
	T/K	η_1	η_2	η_3/Pa s
PAA[a)]	395.15	0.0092	0.0024	0.0034
MBBA[b)]	298.15	0.1361	0.0240	0.0413
HBAB[c)]	333.15	0.0960	0.0175	0.0290

a) Ref. 14. b) Ref. 17. c) Ref. 16.

Table 2. Comparison of theoretical prediction with experiment[a)]

	T/K	ν_{theory}	$\frac{D_{//\text{theory}}}{D_{//\text{expt}}}$	$\frac{D_{\perp\text{theory}}}{D_{\perp\text{expt}}}$	$\frac{(D_{//}/D_{\perp})_{\text{theory}}}{(D_{//}/D_{\perp})_{\text{expt}}}$
PAA	395.15	3.49	6.5×10^{-10}	5.5×10^{-10}	1.2
			4.1×10^{-10}	3.2×10^{-10}	1.3
MBBA	298.15	3.85	4.4×10^{-11}	3.1×10^{-11}	1.4
			1.2×10^{-10}	9.0×10^{-11}	1.3
HBAB	333.15	3.86	3.9×10^{-11}	2.9×10^{-11}	1.4
			(2.7×10^{-10})	1.7×10^{-10}	(1.6)

a) Diffusion coefficients are given in units of m^2 s^{-1}. Experimental data of the diffusion coefficients are quoted from Ref. 19 (^{14}C-tracer) for PAA, from Ref. 20 (NMR pulsed field gradient) for MBBA, and from Ref. 21 (NMR relaxation) for HBAB. The data $D_{//}$ and $D_{//}/D_{\perp}$ of HBAB are less reliable because $D_{//}/D_{\perp} \to 2.0$ in the low temperature limit was assumed to derive them.

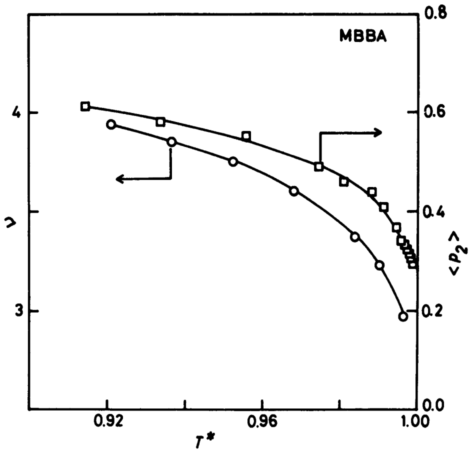

Fig. 3. Effective anisotropy factor ν of a molecule (○), and orientational order parameter $\langle p_2 \rangle$ (□) in MBBA as a function of reduced temperature, $T^* = T/T_c$. The ν was calculated from the data of Ref. 17 by using Eq. 12; the $\langle p_2 \rangle$ was taken from Ref. 22.

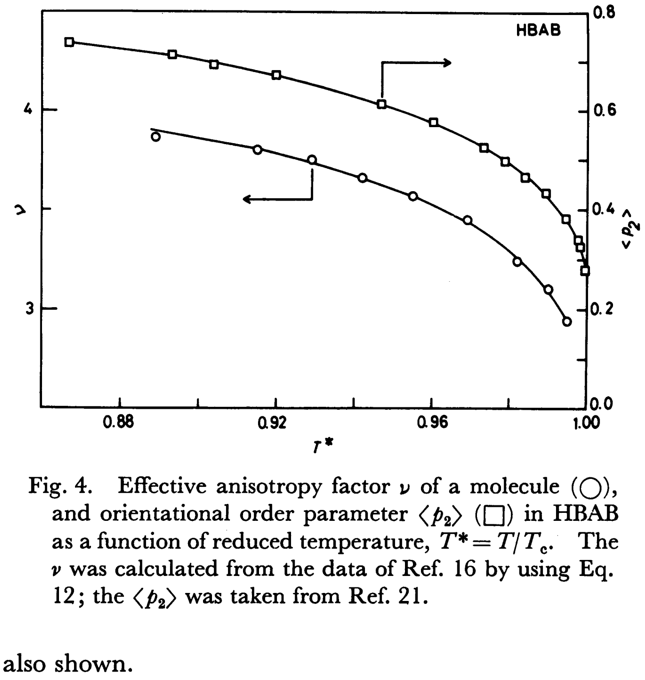

Fig. 4. Effective anisotropy factor ν of a molecule (○), and orientational order parameter $\langle p_2 \rangle$ (□) in HBAB as a function of reduced temperature, $T^* = T/T_c$. The ν was calculated from the data of Ref. 16 by using Eq. 12; the $\langle p_2 \rangle$ was taken from Ref. 21.

According to our model, ν calculated from η_1 and η_3 is a measure of the effective geometrical anisotropy of a molecule at each temperature, and should exhibit the temperature-dependence that resembles that of $\langle p_2 \rangle$ because $\langle p_2 \rangle$ is defined as the ensemble average of the second rank Legendre polynomial

$$\langle p_2 \rangle = \langle p_2(\cos\Theta) \rangle = \frac{1}{2}\langle 3\cos^2\Theta - 1 \rangle,$$

where Θ is the angle between $\boldsymbol{n}$ and the instantaneous molecular axis. In other words, both ν and $\langle p_2 \rangle$ are some motional average of the shape of molecular volume. The asymptotic value of ν in the low temperature limit, *i.e.*, on the condition $\langle p_2 \rangle = 1$ will be identical with ν derived on the basis of static molecular structure. The results of calculation given in Figs. 3 and 4 and Table 2 show that these are in fact the case: The ν_0, asymptotic value of ν in the low temperature limit, are

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††† The data on the temperature-dependences of η_1 and η_3 of PAA are not available to the authors.

$$\nu_0 = 4.2 \pm 0.1 \text{ for MBBA,}$$

and

$$\nu_0 = 4.1 \pm 0.1 \text{ for HBAB.}$$

The ν of PAA is smaller than the ν of the other two compounds, corresponding to the fact that only PAA does not have an end chain. Thus, the calculated value of ν for the three compounds reflect their static molecular structure well in their relative as well as the absolute magnitude. The temperature dependence of ν in the two compounds has good parallelism to that of $\langle p_2 \rangle$.

We can thus conclude that the quantity ν derived from the "pencil model" has a clear physical significance as an effective anisotropy factor of a molecule in the nematic liquid crystalline state.

Self-diffusion Coefficient Tensor. Experimental data on self-diffusion coefficient tensor known until now[19,20] has revealed that its anisotropy, $D_{//}/D_{\perp}$, is not strongly dependent on material, and that $D_{//}/D_{\perp} \approx 1.4 \pm 0.2$ holds except in the close vicinity of T_c. The value κ, the only adjustable parameter in our theory is estimated to be $\kappa \approx 0.4$ by utilizing Eq. 13 and the viscosity data.

The principal values of the tensor $\boldsymbol{D}$ can now be calculated by using Eqs. 9—11 and the viscosity data (Table 1), and by assuming $\kappa = 0.4$. The value of a was taken from the X-ray work[23] ($\sqrt{3}\ a = 0.50$ nm, for all materials). The results of the calculation are tabulated and compared with the experimental data in Table 2. The agreements are satisfactory.

Kneppe-Schneider-Sharma's Empirical Law on η_3/η_2. Kneppe, *et al.*[11] pointed out recently that the quantity η_3/η_2 is almost independent of temperature, and has a relatively constant value irrespective of the material. The η_3/η_2 for MBBA and HBAB are shown in Fig. 5, which confirms that empirical law. The law is interesting as the quantity η_3/η_1, on the contrary, exhibits strong dependence on temperature as discussed above.

This law can be rationalized by our model. By rewriting Eqs. 12 and 13, the relations

$$\frac{\eta_3}{\eta_1} = \frac{9}{2\nu^2} \tag{14}$$

and

$$\frac{\eta_3}{\eta_2} = 3\kappa \frac{D_{//}}{D_{\perp}} \tag{15}$$

follow. Strongly temperature-dependent factor ν does not appear in Eq. 15. One can see that the empirical law by Kneppe *et al.* is consistent with the well-accepted knowledge[6] that the diffusion anisotropy $D_{//}/D_{\perp}$ is not strongly dependent on either material or temperature. If we take a rough approximation that diffusion anisotropy is independent of temperature, *i.e.*, $D_{//}/D_{\perp} = 1.40$ and taking $\kappa = 0.40$, Eq. 15 gives

$$\frac{\eta_3}{\eta_2} = 1.68, \tag{16}$$

which is in fair agreement with experiment as is seen in Fig. 5. The residual small dependence of η_3/η_2 on temperature will be attributed to the temperature-dependence of $D_{//}/D_{\perp}$.

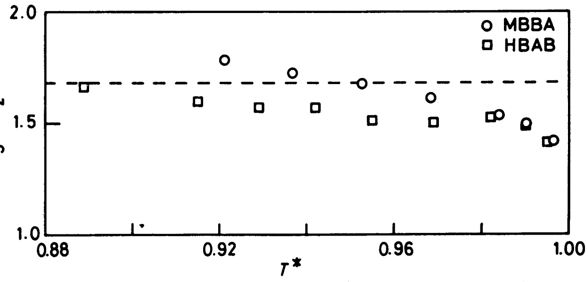

Fig. 5. The η_3/η_2 for MBBA (○), and for HBAB (□) as a function of reduced temperature. The dashed line represents Eq. 16.

In conclusion, it has been demonstrated that the properties of viscosity and self-diffusion in the nematic liquid crystals can be explained fairly well by using the "pencil model," a simple model which is based on the geometrical characteristic of the constituent molecule and which involves only one adjustable parameter κ ($\kappa = 0.4$ is universally adopted in this paper).

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